



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : H01M 10/40, C07C 311/48		A1	(11) International Publication Number: WO 99/30381 (43) International Publication Date: 17 June 1999 (17.06.99)
<p>(21) International Application Number: PCT/US98/11708</p> <p>(22) International Filing Date: 5 June 1998 (05.06.98)</p> <p>(30) Priority Data: 08/988,507 10 December 1997 (10.12.97) US</p> <p>(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).</p> <p>(72) Inventors: LAMANNA, William, M.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). LOCH, Robert, B.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).</p> <p>(74) Agents: SCHULTE, Daniel, C. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: BIS(PERFLUOROALKYLSULFONYL)IMIDE SURFACTANT SALTS IN ELECTROCHEMICAL SYSTEMS</p>			
<p>(57) Abstract</p> <p>Electrolyte compositions and electrochemical systems containing such compositions are described where the electrolyte includes in a matrix material a combination of a conductive salt and a bis(perfluoroalkylsulfonyl)imide surfactant salt. The compositions improve wettability of electrodes and separators while maintaining and improving conductivity, stability, and compatibility with other cell components.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NB	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

**BIS(PERFLUOROALKYLSULFONYL)IMIDE
SURFACTANT SALTS IN ELECTROCHEMICAL SYSTEMS**

Field of the Invention

5 This invention relates to bis(perfluoroalkylsulfonyl)imide surfactant salts which, when used in electrolytes, enable the electrolytes to quickly and effectively wet the electrodes and separator of an electrochemical system.

Background of the Invention

10 In recent years, highly conductive lithium salts such as lithium perchlorate, lithium hexafluorophosphate, lithium tetrafluoroborate, lithium hexafluoroarsenate and lithium trifluoromethanesulfonate, lithium bis(trifluoromethanesulfonyl)imide, lithium bis(perfluoroethanesulfonyl)imide and lithium tris(trifluoromethanesulfonyl)methide have found frequent use in liquid, polymer 15 and gel electrolytes for lithium primary and secondary batteries. See, for example, Kirk-Othmer's *Encyclopedia of Chemical Technology*, Fourth Edition, 3, 1016-1018 (1992) and 1107-1109; and 15, 446-447 (1995). Typically, liquid electrolytes for lithium batteries are made by dissolving lithium salt(s) of choice in anhydrous polar aprotic liquid solvent(s) at a Li⁺ molar concentration of around 20 0.5-2.0M to produce a homogeneous solution having good conductivity and stability. The solvent must be sufficiently polar to effectively dissolve and dissociate the electrolyte salt, yet the solvent must be aprotic, i.e., free of any active hydrogen, to prevent reaction with the anode, which contains lithium metal or a form of carbon, such as graphite, intercalated with lithium. Liquid electrolytes 25 are often very viscous, due to extensive polar interaction, and have a very high surface tension, exceeding 40 dynes/cm.

 The liquid electrolyte is normally imbibed into the battery during the last part of its construction, and it is desirable that the electrodes and separator be quickly and thoroughly wet by the electrolyte so as to facilitate rapid battery 30 manufacturing and to optimize battery performance. However, due to high viscosity and surface tension, the liquid electrolyte often cannot wet the separator or composite electrodes quickly and effectively. Separators are typically

constructed from microporous polyolefin films which can have a surface energy as low as 30-35 dynes/cm. Electrodes are also frequently constructed from hard-to-wet (i.e., low surface energy) materials, including polytetrafluoroethylene and polyvinylidene fluoride binders. The very small size and tight construction of most 5 lithium batteries (typically button, jelly-roll or prismatic configurations) further aggravates the wetting problem.

The relative surface energy between a liquid and a porous solid is very important in determining the wetting properties of the liquid. A liquid with a surface energy higher than the surface energy of the solid substrate will not wet 10 the solid. The liquid will bead on the surface of the solid. A liquid with a surface energy approximately equal to the surface energy of the solid substrate will wet the solid but at a slow rate of penetration and will only penetrate the larger pores of the solid. A liquid with a surface energy lower than that of the solid substrate will rapidly wet the solid and penetrate substantially all of the open porosity of 15 the solid. Therefore in order to effect complete and rapid wetting of the separator and electrode materials of a battery, the surface energy of the liquid should be less than the surface energy of the solid materials. These wetting properties apply not only to pure liquids but also to materials with liquid phases such as plasticized polymers.

Many trade-offs are made in battery design and process engineering in 20 order to accommodate the necessity of a complete and rapid electrolyte fill operation. For example, the electrodes cannot be manufactured to minimize porosity because at some point the pore size will be too small to be effectively wetted by electrolyte. Yet the lower the porosity of the electrode the more active 25 material that can be packed into the cell and the higher the resulting energy of the battery. As a result, increasing the wetting properties of an electrolyte will allow the use of electrodes with higher density and energy.

Many of the electrolyte formulations available have a surface energy which 30 is too high to spontaneously wet the battery components. These formulations must be compromised with suitable solvents, which decrease the performance characteristics of the battery. The use of a surfactant will allow the use of electrolyte solvent formulations not previously accessible to the battery engineer.

Special process techniques are sometimes employed such as vacuum or pressure to accelerate the wetting of components by the electrolyte. Increasing the wetting, properties of the electrolyte can minimize or eliminate these techniques and can decrease the time necessary for the electrolyte fill operation.

5 The availability of a compatible surfactant salt opens up a wider range of operating parameters for the battery engineer in the design and manufacture of components, selection of materials, and formulation of electrolytes.

10 Conventional surfactants which aid electrolyte wetting can have an adverse effect on cell performance, due to their inherent thermal or redox instability, their interference with conductivity, or their incompatibility with other cell components such as the anode, cathode or current collector.

15 Razaq et al., in *J Electrochem. Soc.* 136, No. 2, February 1989, reports the effects of a sulfonimide, $\text{CF}_3\text{SO}_2\text{NHSO}_2\text{C}_4\text{F}_9$, as an additive to 85% phosphoric acid electrolyte in hydrogen-oxygen fuel cells to increase oxygen solubility near the catalyst and thereby increase the rate of oxygen reduction kinetics. In one experiment, the $\text{CF}_3\text{SO}_2\text{NHSO}_2\text{C}_4\text{F}_9$, formed a layer at the electrode/electrolyte interface, reducing the activity of the phosphoric acid and increasing oxygen reduction at the electrode.

20 Thus, there remains a need to improve the wetting of battery electrodes and separators by a non-aqueous liquid electrolyte while maintaining the desired stability and compatibility of the liquid electrolyte with other cell components.

Summary of the Invention

25 We have found that use of certain fluorinated imide surfactant salts in electrolyte compositions exhibits improved wetting of electrodes and separators while maintaining and/or improving conductivity, stability and compatibility with other cell components in electrochemical systems, such as batteries, double-layer capacitors, fuel cells, electroplating, electrorefining and the like.

30 Accordingly, the present invention provides for an improved electrolyte composition in a matrix material which includes:

- (a) a conductive salt, and
- a surfactant salt of the formula



wherein M^{+n} is a cation with a valence equal to n;

n is from 1 to 4;

5 R_f is a straight or branched perfluoroalkyl group of 1 to 12 carbon atoms, a perfluorocycloalkyl group or a perfluorocycloalkyl perfluoroalkyl group of 4-7 ring carbon atoms and 1-4 carbon atoms on the alkyl chain, which perfluoro(cyclo)alkyl, or perfluoroalkyl chain may optionally contain catenary heteroatoms; and

10 R_f' is a straight or branched perfluoroalkyl group of 1 to 8 carbon atoms, a perfluorocycloalkyl group or a perfluorocycloalkyl perfluoroalkyl group of 4-7 ring carbon atoms and 1-4 carbon atoms on the alkyl chain, which perfluoro(cyclo)alkyl, or perfluoroalkyl chain may optionally contain catenary heteroatoms. wherein R_f and R_f' have a total of at least 5 carbon atoms; and
15 wherein the molar ratio of conductive salt to surfactant salt is between about 99.9:0.1 to about 75:2;

In a second aspect, the invention features an electrochemical system that includes at least one positive electrode, at least one negative electrode, and an electrolyte in a matrix material comprising the combination of a conductive salt and a surfactant salt of formula I as described above, where the molar ratio of 20 conductive salt to surfactant salt may range between about 99.9:0.1 to 75:25, preferably between about 99:1 to 90: 1 0.

A third aspect of the invention includes a method of improved wetting of electrodes and separators in electrochemical systems by incorporating into an electrolyte composition in a matrix material containing a conductive salt up to 25 mole %, based on total salt content, of a fluorinated imide surfactant of formula I as described above.

We have found that by adding a surfactant salt of the present invention to a conductive salt in an electrolyte composition, one or more of the following advantages can result:

- 30 • provides all of the requisite functions of a battery electrolyte salt including: solubility, ionic conductivity, chemical and thermal stability, etc.;

- lowers the surface tension of the resulting electrolyte solution;
- allows wetting of battery component materials such as separators and electrodes which would not normally wet-out in available solutions;
- expands the range of electrolyte compositions available by allowing
5 the use of -high viscosity, high surface energy solvents;
- allows more rapid wetting of battery components to save time, process steps. and process equipment;
- increases the area of contact between the electrolyte and the
10 electroactive materials to decrease battery internal resistance and increase performance;
- can be used in small quantity additions to existing electrolyte formulations to enhance performance; and
- provides for potential applications in a variety of battery systems
15 including aqueous electrolyte batteries as well as fuel cells and capacitors.

Brief Description of the Drawings

FIGURE 1 is a cut-away view of a lithium-ion battery.

FIGURE 2 is a plot of discharge capacity as a function of cycle number.

20 FIGURE 3 is a plot of discharge capacity as a function of current density or rate of discharge.

Detailed Description

The present invention relates to liquid electrolyte compositions useful in
25 electrochemical systems such as batteries, e.g. primary and secondary (rechargeable) batteries, double-layer capacitors, supercapacitors, fuel cells, electroplating and electrorefining systems and the like. The electrolyte compositions include solutions of certain fluorinated imide surfactant salts in a matrix material which exhibit improved wetting of electrodes and separators along
30 with good conductivity, stability and compatibility with other cell components.

The fluorinated imide surfactant salts useful in this invention are depicted in Formula I:



wherein:

M^{+n} is a cation with valence equal to n,

5 n is from 1 to 4;

R_f is a straight or branched perfluoroalkyl group of 1 to 12 carbon atoms, preferably 4 to 12 carbon atoms, a perfluorocycloalkyl group or a perfluorocycloalkyl perfluoroalkyl group of 4-7 ring carbon atoms and 1-4 carbon atoms on the alkyl chain, and which perfluoro(cyclo)alkyl or 10 perfluoroalkyl chain may also contain catenary heteroatoms such as oxygen and nitrogen; and

15 R_f' is a straight or branched perfluoroalkyl group of 1 to 8 carbon atoms, a perfluorocycloalkyl group or a perfluorocycloalkyl perfluoroalkyl group of 4-7 ring carbon atoms and 1-4 carbon atoms on the alkyl chain, and which perfluoro(cyclo)alkyl or perfluoroalkyl chain may also contain catenary 20 heteroatoms such as oxygen and nitrogen.

Wherein the sum of carbon atoms in the R_f and R_f' chains must be at least 5 and is preferably at least 8, and more preferably R_f contains at least 8 carbon atoms.

20 Preferably, M^{+n} is a cation of an alkali metal, an alkaline earth metal, a transition metal. A rare earth metal, a Group IIB metal or a Group IIIB metal, a tetraalkylammonium cation, or a proton: more preferably, M^{+n} is a cation of an alkali metal, most preferably, M^{+n} is a lithium cation.

Suitable fluorinated lithium 'unide' surfactant salts include

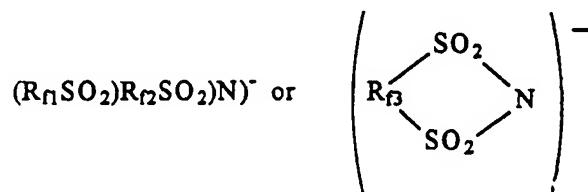
25 $(C_8F_{17}SO_2)N^+(SO_2CF_3)Li^+$, $(C_4F_9SO_2)_2NLi^+$, $(C_8F_{17}SO_2)N(SO_2C_4F_9)Li^+$, $(C_8F_{17}SO_2)_2NLi^+$, $(C_4F_9SO_2)N(SO_2C_3F_7)Li^+$ and $(C_4F_9SO_2)N^+(SO_2CF_3)Li^+$. Other cations may replace the lithium cation, such as Na^+ , Ca^{+2} , Ba^{+2} , Al^{+3} , La^{+3} , Eu^{+3} , Sm^{+3} $(C_2H_5)_4N^+$, $(CH_3)_4N^+$ and H^+ .

30 The electrolyte composition of the present invention includes a conductive salt different from the surfactant salt. Typically any conventional conductive salt known for electrochemical systems may be used. For example, a conductive salt may include:

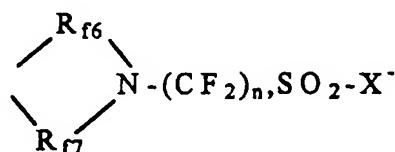
a cation selected from the group consisting of an alkali metal; an alkaline earth metal; a Group IIB metal; a Group IIIB metal; a transition metal; a rare earth metal; an ammonium cation such as tetraalkylammonium and trialkylammonium; and a proton; and

- 5 an anion selected from the group consisting of NO_3^- , Br^- , Γ , BF_4^- , PF_6^- , AsF_6^- , ClO_4^- , SbF_6^- and $\text{R}_f^0\text{SO}_3^-$; in which R_f^0 is a perfluoroalkyl group having between 1 and 12 carbon atoms;

an anion of the formula

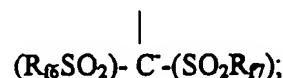


- 10 in which R_{f1} and R_{f2} are each independently a straight or branched perfluoroalkyl group of 1 to 12 carbon atoms, preferably of 1 to 3 carbon atoms; and R_{f3} is a perfluoroalkylene moiety of 2 to 4 carbon atoms optionally substituted by a straight or branched perfluoroalkyl group of 1 to 2 carbon atoms, with R_{f3} having a total of up to 6 carbon atoms;
- 15 an anion having a formula $\text{R}_{f4}\text{R}_{f5}\text{N}-(\text{CH}_2)_n\text{SO}_2\text{-X}^-$



in which X^- is $-\text{O}^-$, $-\text{NSO}_2\text{R}_{f8}$, or

20

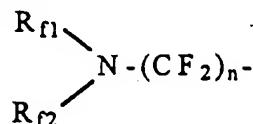


Z is $-\text{CF}_2^-$, $-\text{O}^-$,

25

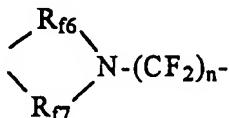


or $-SF_4^-$; R_{f4} and R_{f5} , independently, are $-C_mF_{2m+1}$, or $-(CF_2)_qSO_2-X$; R_{f6} and R_{f7} , independently, are $-C_mF_{2m+1}$, $-(CF_2)_qSO_2-X$,

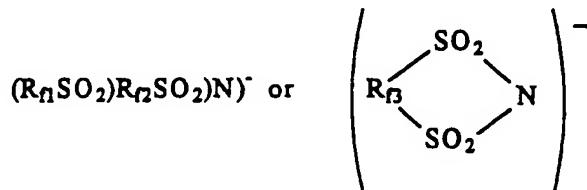


or

5



- R_{f8} is $-C_mF_{2m+1}$, or $-(CF_2)_qSO_2-X$; R_{f5} and R_{f7} , independently, are perfluoroalkylene moieties having the formula $-C_rF_{2r}$; n' is 1-4; r is 1-4; m is 1-12 preferably 1-8; and q is 1-4; a bis-fluoroalkylsulfonyl methide anion $R_f^{II}-SO_2-C^-(R)-SO_2-R_f^{III}$ in which R_f^{II} and R_f^{III} , independently, are perfluoroalkyl groups having between 1 and 12 carbon atoms, and X is H, Br, Cl, I, an alkyl group having between 1 and 20 carbon atoms, aryl, or alkaryl;
- 10 and a tris-(perfluoroalkylsulfonyl)methide anion of the formula $C(SO_2R_f^{II})(SO_2R_f^{III})(SO_2R_f^{IV})$ in which R_f^{II} , R_f^{III} , and R_f^{IV} , independently, are perfluoroalkyl groups having between 1 and 12 carbon atoms, preferably between 1 and 4 carbon atoms.
- 15 A more preferred conductive salt includes one that has a PF_6^- , ClO_4^- , AsF_6^- , BF_4^- , or $(CF_3SO_2)_3C^-$ anion, or has an anion of the formula:



- 20 or has an anion of the formula:



in which R_{f1} , and R_{f2} are each independently a straight or branched perfluoroalkyl group of 1 to 3 carbon atoms, with R_{f1} , and R_{f2} having a total of up to 4 carbon atoms;

R_f is a perfluoroalkylene moiety of 2 to 4 carbon atoms optionally

- 5 substituted by a straight or branched perfluoroalkyl group of 1 to 2 carbon atoms, with R_f having a total of up to 6 carbon atoms; and

R_f^V is a perfluoroalkyl group having from 1 to 4 carbon atoms.

- Most preferred conductive salts are lithium hexafluorophosphate, lithium bis(trifluoromethane-sulfonyl)imide, lithium tetrafluoroborate, lithium perchlorate, 10 lithium hexafluoroarsenate, lithium trifluoromethylsulfonate, lithium tris(trifluoromethanesulfonyl)methide or a mixture thereof.

- In general, the above described low and high molecular weight bis(perfluoroalkylsulfonyl)imide and cyclic perfluoroalkylenedisulfonylimide conductive and surfactant salts can be prepared from the reaction of 15 perfluoroalkylsulfonyl fluorides, e.g. R_fSO_2F , or perfluoroalkylenedisulfonyl fluoride, $FSO_2R_fSO_2F$, with anhydrous ammonia. Symmetrical imides in which R_f and R_f' and R_{f1} , and R_{f2} , are the same can be prepared in a single step using a non-nucleophilic base such as triethylamine as shown in Scheme I, whereas unsymmetrical imides in which R_f and R_f' and R_{f1} and R_{f2} are different must be 20 prepared in two steps as shown in Scheme II.

SCHEME I



SCHEME II

25



Cyclic perfluoroalkylenedisulfonylimide salts can be prepared as described U.S. Pat. No. 4,387,222, incorporated herein by reference.

Perfluoroalkanesulfonyl fluorides and perfluoroalkylenedisulfonyl fluorides used as precursors to the imide salts of this invention can be prepared by a variety 5 of methods known in the art as described, for example, in U.S. Pat. Nos. 3,542,864; 5,318,674; 3,423,999, 3,951,762; 3,623,963; 2,732,398 and S. Temple, *J. Org. Chem.*, 33(1), 344(1968), D.D. DesMarteau, *Inorg. Chem.* 32, 5007 (1993), all of which are incorporated herein by reference.

To form the electrolyte composition, the conductive and surfactant salts are 10 mixed with the matrix material such that the salts are at least partially dissolved or dispersed in the matrix material. The salts are preferably employed at a concentration such that the conductivity of the electrolyte solution is at or near its maximum value, although a wide range of other concentrations will also serve.

The matrix material may be in the form of a solid, liquid, gel or a liquid 15 impregnated porous membrane. For battery applications, the matrix material is chosen to provide the particular conductance, viscosity, mechanical strength, reactivity and stability desired for the electrolyte.

Suitable matrix materials for preparing electrolyte solutions can be liquid, polymeric or mixtures of polymer and liquid. Examples of suitable solid matrix 20 materials include polymers and copolymers such as polyethers like poly(ethylene oxide), polyesters, polyacrylates, polyphosphazenes, polysiloxanes, poly(propylene oxide), fluoropolymers (e.g., poly(vinylidene fluoride)), and poly(acrylonitrile), as well as the polymers and copolymers described in Armand et al., U.S. Pat. No. 4,505,997, incorporated herein by reference, and mixtures thereof. The polymers 25 may be used in cross-linked or uncross-linked form and plasticized. Such materials are generally dry, have a water content less than about 100 ppm, preferably less than about 50 ppm.

Mixtures of matrix materials can be employed and are sometimes preferred in tailoring the matrix material's properties to provide optimum performance. In 30 general, the amount of matrix material is selected such that the total salt concentration ranges from about 0.1 M (moles per liter) to about 2.0M, preferably about 1M. Preferably, the conductive salt concentration in the electrolyte is from

about 0.5 to 1.5M, and the surfactant salt concentration in the electrolyte is from about 10 to 250 millimoles per liter.

In batteries comprising a highly reducing electrode (such as lithium metal) and a liquid matrix material, the liquid is preferably a nonaqueous, polar, aprotic, 5 organic solvent. Such liquids are generally dry, i.e., have a water content less than about 100 ppm, preferably less than about 50 ppm. Examples of suitable aprotic liquids include linear ethers such as diethyl ether, diethylene glycol dimethyl ether, and 1,2dimethoxyethane; cyclic ethers such as tetrahydrofuran, 2-methyltetrahydrofuran, dioxane, dioxolane, and 4-methyldioxolane; esters such as 10 methyl formate, ethyl formate, methyl acetate, dimethyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, and butyrolactones (e.g., gamma butyrolactone); nitriles such as acetonitrile and benzonitrile; nitro compounds such as nitromethane or nitrobenzene; amides such as N,N-dimethylformamide, N,N-diethylformamide, and N-methylpyrrolidinone; 15 sulfoxides such as dimethyl sulfoxide; sulfones such as dimethylsulfone-tetramethylene sulfone, and other sulfolanes; oxazolidinones such as N-methyl-2-oxazolidinone and mixtures thereof. Maximum conductivities of the electrolyte salts of this invention in typical nonaqueous, polar, aprotic liquid media (e.g., propylene carbonate) are generally in the range of 0. 1-20 mS (millisiemens) at 20 room temperature, preferably greater than 1 mS.

A preferred electrochemical system of the present invention relates to a battery that includes at least one cathode, at least one anode, a separator and liquid electrolyte comprising certain fluorinated imide surfactant salts, conductive salts and aprotic solvents.

25 The electrodes (i.e., anode and cathode) of, for example, a lithium battery generally consist of a metallic foil or particles of active material blended with a conductive diluent such as carbon black or graphite bound into a plastic material binder. Typical binders include polytetrafluoroethylene, polyvinylidene fluoride, ethylene-propylene-diene (EPDM) terpolymer, and emulsified styrene-butadiene 30 rubber (SBR), and the binder may be cross-linked. The binder may also be, for example, a solid carbon matrix formed from the thermal decomposition of an organic compound. The metallic foil or composite electrode material is generally

applied to an expanded metal screen or metal foil (preferably aluminum, copper or nickel) current collector using a variety of processes such as coating, casting, pressing or extrusion.

Examples of suitable battery anodes include lithium metal, lithium metal alloys, sodium metal, carbon-based materials such as graphite, coke, carbon fiber, pitch, transition metal oxides (such as $\text{LiTi}_3\text{O}_{12}$ and LiWO_2), and lithiated tin oxide. In the case of lithium ion batteries, the lithium may be intercalated into a host material such as carbon (i.e., to give lithiated carbon) or carbon alloyed with other elements (such as silicon, boron and nitrogen), a conductive polymer, or an inorganic host that is intercalatable (such as $\text{Li}_x\text{Ti}_3\text{O}_{12}$). The material comprising the anode may be carried on foil (e.g., nickel and copper) backing or pressed into expanded metal screen and alloyed with various other metals.

Examples of suitable cathode materials include graphite, amorphous carbon, Li_xCoO_2 , Li_xNiO_2 , Co-doped Li_xNiO_2 , $\text{Li}_x\text{Mn}_2\text{O}_4$, Li_xMnO_2 , V_2O_5 , V_6O_{13} , LiV_3O_8 , $\text{Ba}_2\text{SmNiO}_5$, SmMnO_3 , $\text{SM}_3\text{Fe}_5\text{O}_{12}$, EuFeO_3 , $\text{EuFe}_5\text{O}_{12}$, EuMnO_3 , LaNiO_3 , La_2CoO_4 and LaMnO_3 (including the charged and discharged forms of these materials), and conducting polymers such as polypyrrole, polysulfides and polyvinylferrocene. In primary batteries, the cathode can be fluorinated carbon (e.g., $(\text{CF})_n$), SO_2Cl_2 , $\text{Ag}_2\text{V}_4\text{O}_{11}$, Ag_2CrO_4 , sulfur, polysulfide, and an O_2 or SO_2 electrode.

Lithium batteries and supercapacitors usually contain a separator to prevent short-circuiting between the cathode and anode. The separator usually consists of a single-ply or multi-ply sheet of microporous polymer (typically polyolefin, e.g., polyethylene, polypropylene, or combinations thereof) having a predetermined length and width and having a thickness of less than 10 mils (0.025 cm). For example, see U.S. Pat. Nos. 3,351,495 (Larson et al.), 4,539,256 (Shipman et al.), 4,731,304 (Lundquist et al.) and 5,565,281 (Yu et al.). The pore size in these microporous membranes, typically about 5 microns in diameter, is sufficiently large to allow transport of ions but is sufficiently small to prevent cathode/anode contact, either directly or from particle penetration or dendrites which can form on the electrodes.

The invention is illustrated further by, but is not intended to be limited to, the following examples.

EXAMPLES

5

SYNTHESIS, SOURCE OF FLUORINATED IMIDE SALTS

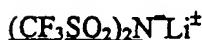


10 $\text{Li}^{\pm}\text{PF}_6^-$ (high purity, battery grade) was purchased from Hashimoto Chemical Co., Ltd. through Biesterfeld U.S., Inc., a U.S. distributor.



Fluorad™ CF-122 Lithium Trifluoromethanesulfonate (available from 3M Co.) was used as the source of $\text{CF}_3\text{SO}_3^-\text{Li}^{\pm}$.

15



Fluorad™ HQ-1 15 Lithium Trifluoromethanesulfonimide (available from 3M Co.) was used as the source of $(\text{CF}_3\text{SO}_2)_2\text{N}^-\text{Li}^{\pm}$.

20 $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-\text{Li}^{\pm}$

$(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-\text{Li}^{\pm}$ was prepared using the procedure described in Example 3 of U.S. Pat. No. 5,652,072, which is herein incorporated by reference.



25 $(\text{C}_4\text{F}_9\text{SO}_2\text{N}^-(\text{SO}_2\text{CF}_3)\text{Li}^-$ was prepared using the procedure described in Example 1 of U.S. Pat. No. 5,652,072, which is herein incorporated by reference.



30 $(\text{C}_8\text{F}_{17}\text{SO}_2\text{N}^-(\text{SO}_2\text{CF}_3)\text{Li}^{\pm}$ was prepared using essentially the same procedure as described in Example 1 of U.S. Pat. No. 5,652,072, except that $\text{C}_8\text{F}_{17}\text{SO}_2\text{F}$ was substituted for $\text{C}_4\text{F}_9\text{SO}_2\text{F}$.

C₄F₉SO₂)N⁻(SO₂C₄F₉)Li⁺

(C₄F₉SO₂)N⁻(SO₂C₄F₉)Li⁺ was prepared using the procedure described in Example 4 of U.S. Pat. No. 5,652,072, which is herein incorporated by reference.

5 BATTERY SEPARATORS

The membranes employed in the following test methods were prepared as follows:

PP1117-19 Membrane Preparation

10 A polypropylene resin, available from Union Carbide under a designation DS 5D45 with a melt -flow index of 0.65 dg./min (ASTM D1238, Condition I), was fed into the hopper of a 40 mm twin-screw extruder. Mineral oil, available under a trade designation Amoco White Mineral Oil #31 and having a viscosity of 60 centistokes (ASTM D445 at 40°C) (available from Amoco Petroleum Products,

15 Oak Brook, Illinois), was introduced into the extruder through an injection port at a rate to provide a composition of 60% by weight of the polymer and 40% by weight mineral oil. The composition also contained 0.28% MilladTM 3905 (available from Milliken & Co., Spartanburg, South Carolina) nucleating agent. The overall feed rate was 11.35 kg/hr. The polymer was heated to 271°C in the extruder to melt

20 and, after mixing with oil, the temperature was maintained at 177°C during the extrusion. The melt was extruded through a 3.8.1 cm-wide coat hanger slit die and cast onto a casting wheel maintained at 60°C. The cast film was extracted with HCFC-123, LVertrelTM 423 (C₂HF₃Cl₂) (duPont) to remove mineral oil. then oriented 2.7 to 1 in the machine direction at 90°C and 1.5 to 1 in the cross-

25 direction at 138°C.

PE 9711 Cotran Membrane Preparation

A polyethylene resin, available from Fina Chemicals under a designation Fina 1285 with a melt flow index of 8 dg/min (ASTM D1238-90, Condition F), 30 was fed into the hopper of a 40 mm twin-screw extruder. Mineral oil, available under a trade designation Witco Protol and having a viscosity of 36 centistokes (ASTM D445 at 40°C) (available from Witco Corp., Greenwich, Connecticut) was

introduced into the extruder through an injection port at a rate to provide a composition of 39% by weight of the polymer and 61% by weight mineral oil. The overall feed rate was 10.7 kg/hr. The polymer was heated to 271°C in the extruder to melt and, after mixing with oil, the temperature was maintained at 204°C during 5 the extrusion. The melt was extruded through a 38.1 cm-wide coat hanger slit die and cast onto a casting wheel maintained at 66°C. The cast film was extracted with HCFC-123 to remove mineral oil, then oriented 2.3 to 1 in the machine direction at 35°C and 2.2 to 1 in the cross-direction at 102°C.

10 PREPARATION OF ELECTRODES

Cathode

A mix was prepared by blending 44 g of LiCoO₂ (FMC, Bessemer City, North Carolina) with 5.0 g of VXC72 conductive carbon (Cabot Corp., Billesica, Massachusetts) and 1.0 c. of Kynar 461 polyvinylidene fluoride resin (Elf Atochem 15 North America, Philadelphia, Pennsylvania) in a small food processor for 2 minutes. The food processor is a small single-speed common household food processor. Portions of the resulting mix were pressed into pellets using a pellet die and a Carver press at about 2000 pounds of force. The pellet die is a steel cylinder body 3 cm diameter by 2.5 cm height with a central bore 7.5 mm in diameter and a 20 steel pin 3.75 cm in length and 7.47 cm in diameter with flat ends. The body of the die was placed on a flat surface and loaded with a measured weight of mix. The pin was inserted and the whole assembly placed in the Carver press. The resulting pellet electrodes averaged 7.6 mm in diameter, 0.28 mm in height and 33 mg in weight.

25 Anode

Anode pellets were prepared in a manner identical to the cathode procedure except that the ingredients of the mix were 21 g of XP3 petroleum coke (Conoco, Ponca City, Oklahoma), 1.2 g of Super S conductive carbon (MMM Carbon, Brussels, Belgium), and 3 g of Kynar 461 polyvinylidene fluoride. The resulting 30 pellet electrodes averaged 7.7 mm in diameter, 0.35 mm in height and 27 mg in weight.

TEST METHODS

Surface Tension

Surface tensions of electrolytes were measured using the Wilhelmy plate method, which utilizes a vertically suspended roughened platinum plate of exactly known geometry. Using this method, the lower edge of the plate is brought into contact with the electrolyte, with the electrolyte "jumping" to (i.e., forming a meniscus along the side of) the plate and pulling the plate into the electrolyte. The Wilhelmy force along the length of the edge caused by this wetting is measured by pulling the plate from the electrolyte until the plate is level to the surface of the electrolyte. The surface tension, in dynes/cm, is then recorded as the force exerted by the electrolyte per length of plate edge contacted.

Coin Cell Charge/Discharge Cycling

To demonstrate electrolyte performance in a real test battery, charge/discharge cycling tests were run with a "1225" size coin cell, measuring capacity using a commercial battery tester available from Maccor Inc., Tulsa, Oklahoma.

The "1225" coin cell stack assembly was constructed as shown in FIG. 1. A stainless steel top 1, 12 mm in diameter, was placed on a horizontal surface flat side down. On this base were stacked in order a 31 mil (0.80 mm) thick copper disk anode current collector 2 and an anode 3 prepared as described above. 40 µl of the test electrolyte solution (consisting of test salt(s) dissolved in a 50/50 (vol) blend of ethylene carbonate/dimethyl carbonate, dried to a water content of no greater than 50 ppm, as determined by Karl Fischer titration) was applied to the graphite side of the anode surface. Then two layers of 99711 polyethylene, 2.2 mils, separator 4 (prepared as described above) were placed on the wet anode surface. A polypropylene spacer gasket 5 was inserted. To complete the assembly, cathode 6 prepared as described above was placed on the stack, 40 µl of additional electrolyte were added, followed by a 20 mil (0.51 mm) thick aluminum disk cathode current collector 7 and a chromium steel can cell 8. The assembly was then crimp sealed to complete the fabrication of the "1225" coin cell.

The constructed "1225" coin cell was then cycled at room temperature using a Maccor® Series 2000 battery tester (available from Maccor Inc., Tulsa

OK) with appropriate current and voltage range operated with generation 3.0 software designed to charge the cell at a current density of no greater than 2 mA/cm² under a constant voltage of 4.2 V, followed by discharge under a constant current of 1mA/cm², With two 30 minute interrupts (i.e., no current flow, circuit 5 opened up) when the cell voltage reached 3.8 V and 3.0 V, respectively; total discharge time was typically 3 hours. Each cell was charged for a minimum of 10 cycles. Every fifth cycle the discharge current was scanned successively from a high of 30 mA/cm² to a low of 0.03 mA/cm² in order to determine the rate 10 capability and the maximum capacity of the cell. The average total cell discharge specific capacity (mAh/g) was plotted vs. cycle number. It is desirable that initial capacity be high and remain high over the entire number of cycles run. The impedance characteristics of the cells before cycling were determined using a 15 Princeton Applied Research Model 271 potentiostat and a Solatron® FRA SI1260 frequency response analyzer equipped with an I1287 electrochemical interphase (both available from Solatron, a Division of Solatron Group Ltd., Houston, TX). Scans were made at an amplitude of 5 millivolts over a frequency range of 100.000 Hz to 0.1 Hz.

Examples 1-4 and Comparative Examples C1-C4

20 The wetting ability of various fluorinated imide surfactant salts, both inside and the outside of this invention, was evaluated by dissolving each salt at 1 molar concentration in a 50/50 (wt) blend of propylene carbonate/ethylene carbonate to form a liquid electrolyte, applying electrolyte to the surface of polyolefin separators, and then measuring contact angles, both initially and after 500 seconds 25 of contact. Separators used were 9711 Cotran polyethylene separator (prepared as above described) and 1117-19D polypropylene separator (prepared as above described). Contact angles were measured using a Kruss G2/G40 Contact Angle Measuring Device (available from Kruss Corp.).

Results from this contact angle evaluation are shown in Table 1.

Table 1

Ex.	Salt	No. of C Atoms:	<u>Polyethylene:</u>		<u>Polypropylene:</u>	
			Init.	500 s.	Init.	500 s.
1	(C ₈ F ₁₇ SO ₂)N(SO ₂ CF ₃)Li ⁺	9	47	0	47	39
2	(C ₄ F ₉ SO ₂)N(SO ₂ C ₄ F ₉)Li ⁺	8	47	0	59	56
3	(C ₄ F ₉ SO ₂)N(SO ₂ CF ₃)Li ⁺	5	41	0	76	69
C1	(C ₂ F ₅ SO ₂)N(SO ₂ C ₂ F ₃)Li ⁺	4	67	65	76	76
C2	(CF ₃ SO ₂)N(SO ₂ CF ₃)Li ⁺	2	87	87	84	84
C3	CF ₃ SO ₃ Li ⁺	1	79	73	83	83
C4	Li ⁺ PF ₆ ⁻	0	77	73	79	79

The data in Table I show that, with the polyethylene separator, the imide salts having at least 5 carbons in their combined perfluorinated chains provided a liquid

5 electrolyte with superior wetting performance, particularly after contact for 500 seconds. A lesser wetting improvement was noted with the polypropylene separator.

Example 5

10 In this study, the two best overall wetting candidates from Table 1, (C₈F₁₇SO₂)N(SO₂CF₃) Li⁺ (Example 1) and (C₄F₉SO₂)N(SO₂C₄F₉)Li⁺ (Example 2), were added incrementally as surfactant salt additives to an electrolyte consisting of 1 M Li⁺ PF₆⁻ in a 50/50 (wt) blend of ethylene carbonate/propylene carbonate. The concentration to achieve a zero contact angle after 500 seconds

15 was determined for the 9711 Cotran polyethylene separator.

For (C₄F₉SO₂)N(SO₂C₄F₉) Li⁺ zero contact angle was achieved at a concentration of 0.2M, a relatively low concentration. However, for (C₈F₁₇SO₂)N-(SO₂CF₃) Li⁺, zero contact angle was achieved at an even lower concentration of 0.06M, indicating that this perfluorinated octyl methyl imide was

20 an especially effective surfactant salt.

Example 6 and Comparative Examples C5 and C6

$(C_8F_{17}SO_2)N^+(SO_2CF_3) Li^+$ surfactant salt was compared to a nonionic hydrocarbon surfactant and no surfactant at all as an additive to a liquid electrolyte to enhance the electrolyte's wetting of a porous polypropylene separator.

- 5 In Example 6, 0.15 g of $(C_8F_{17}SO_2)N^+(SO_2CF_3) Li^+$ was added to 5 g of a 1 M solution of $(CF_3SO_2)N^+(SO_2CF_3) Li^+$ (HQ-115) in anhydrous propylene carbonate. 3 drops of the resulting solution were placed on a CelgardTM 2400 porous polypropylene separator (available from Hoechst Celanese Corp., Charlotte, North Carolina). The drops initially beaded up but gradually penetrated the pores of the
10 separator, causing the separator to change in appearance from opaque to translucent.

In Comparative Example C5, the same experiment was run as in Example 5 except that TritonTM DF-12 (a modified polyethoxylated straight chain alcohol having an HLB of 10.6 and known to be a good hydrocarbon surfactant wetting agent available from Union Carbide Corp., Danbury, Connecticut) was used in place of the $(C_8F_{17}SO_2)N^+(SO_2CF_3) Li^+$. The drops remained beaded up, indicating poor wetting.
15

In Comparative Example C6, the same experiment was run as in Example 5 except that no surfactant was added. The drops remained beaded up, indicating
20 poor wetting.

Examples 7-9 and Comparative Examples C7-C9

In Examples 7-9, $(C_8F_{17}SO_2)N^+(SO_2CF_3) Li^+$ was added at 0.1 M concentration to 1 M LiPF₆ in (1) a 50/50 (vol) blend of propylene
25 carbonate/dimethoxyethane, (2) a 50/50 (vol) blend of ethylene carbonate/dimethyl carbonate and (3) 100% propylene carbonate, respectively. Surface tensions of each surfactant solution in electrolyte were measured and recorded using the Wilhelmy plate method.

In Comparative Examples C7-C9, the same experiments were run as in
30 Examples 7-9 except no $(C_8F_{17}SO_2)N^+(SO_2CF_3) Li^+$ was added to the 1 M LiPF₆ electrolytes.

Results from these experiments are presented in Table 2.

Table 2

<u>Example</u>	<u>Surfactant ?</u>	<u>Solvent</u>	<u>Surface Tension (dynes/cm)</u>
7	Yes	PC/DME	28.7
C7	No	PC/DME	33.8
8	Yes	EC/DMC	27.3
C8	No	EC/DMC	39.5
9	Yes	PC	31.2
C9	No	PC	43.7

The data in Table 2 shows that $(C_8F_{17}SO_2)N^+(SO_2CF_3)Li^+$ was able to significantly lower the surface tension of a variety of electrolytes.

5

Example 10 and Comparative Examples C10 and C11

Duplicate coin cell charge/discharge cycling tests were run for 60 cycles with a liquid electrolyte comprising 1 M $Li^+PF_6^-$ in propylene carbonate (1) alone (Comparative Example C10), (2) with 0.1 M $(C_8F_{17}SO_2)N^+(SO_2CF_3)Li^+$ (Example 10), and (3) with a combination of 0.1 M $(C_8F_{17}SO_2)N^+(SO_2CF_3)Li^+$ and 5% (wt) Triton™ DF-12 surfactant (Comparative Example C11). Results, presented in FIG. 2, show that the straight $LiPF_6$ in propylene carbonate electrolyte fails to achieve full cell capacity over the first several cycles whereas the addition of $(C_8F_{17}SO_2)N^+(SO_2CF_3)Li$ alone as an additive provides cells with high initial capacity and does not adversely affect the subsequent cycling performance. However, the $(C_8F_{17}SO_2)N^+(SO_2CF_3)Li^+$ / Triton™ DF-12 blend showed degraded capacity both initially and after cycling, indicating that the hydrocarbon surfactant wetting agent was deleterious to both the initial and the long-term performance of the coin cell.

20

Example 11 and Comparative Examples C12 and C13

Rate capacity curves were also generated from measurements of cumulative capacity (mAh) vs. current density (mA/cm²) of the three coin cells described in Example 10 and Comparative Examples C10 and C11, respectively. These curves,

presented in FIG. 3, show no significant difference in rate capacity behavior with and without the $(C_8F_{17}SO_2)N^+(SO_2CF_3)Li^+$ alone. However, the $(C_8F_{17}SO_2)N^-(SO_2CF_3)Li^+$ / Triton™ DF-12 blend showed decreased rate capacity behavior.

The impedance characteristics of the cells in Example 10 and Comparative

5 Example 10C further illustrate the benefit of the surfactant on the initial cell condition. The average and range cells each) of the high frequency pure component of resistance is reported in Table 3 as ohmic resistance. As the surface area of contact between the electrolyte and the electrode increases resistance decreases, just as the electrical resistance of a wire decreases as its diameter

10 increases. Greater penetration of electrolyte into the electrode and thus greater surface area of contact is reflected in the lower average cell resistance. Further, the much lower range of values obtained with the surfactant reflects the greater stability of that system.

15

Table 3

<u>Example</u>	<u>Salt</u>	<u>Ohmic Resistance</u> <u>Average (Ohms)</u>	<u>Ohmic Resistance</u> <u>Range (Ohms)</u>
10	1M LiPF ₆ + 0.1M $(C_8F_{17}SO_2)N(SO_2CF_3)L$	11	1
C10	1M LiPF6	72	67

WE CLAIM:

1. An electrolyte composition in a matrix material comprising:

(a) a conductive salt, and

(b) a surfactant salt of the formula $((R_fSO_2)(R'_fSO_2)N^-)_nM^{+n}$

5 wherein M^{+n} is a cation with a valence equal to n;

n is from 1 to 4;

R_f is a straight or branched perfluoroalkyl group of 1 to 12 carbon atoms, a perfluorocycloalkyl group or a perfluorocycloalkyl perfluoroalkyl group of 4-7 ring carbon atoms and 1-4 carbon atoms on the alkyl chain, which perfluoroalkyl 10 or perfluorocycloalkyl chain may optionally contain catenary heteroatoms; and

15 R_{f'} is a straight or branched perfluoroalkyl group of 1 to 8 carbon atoms, a perfluorocycloalkyl group or a perfluorocycloalkyl perfluoroalkyl group of 4-7 ring carbon atoms and 1-4 carbon atoms on the alkyl chain, which perfluoroalkyl or perfluorocycloalkyl chain may optionally contain catenary heteroatoms, wherein R_f and R_{f'} have a total of at least 5 carbon atoms; and

wherein the molar ratio of conductive salt to surfactant salt is between about 99.9:0.1 to about 75:25.

20 2. The composition of claim 1, wherein the conductive salt is different from the surfactant salt.

25 3. The composition of claim 1, wherein R_f is a straight or branched perfluoroalkyl group of 4 to 12 carbon atoms, and R_{f'} is a straight or branched perfluoroalkyl group of 1 to 8 carbon atoms.

4. The composition of claim 1, wherein R_f and R_{f'} have a total of at least 8 carbon atoms.

30 5. The composition of claim 1, wherein R_f has at least 8 carbon atoms.

6. The composition of claim 1, wherein the surfactant salt has a cation M⁺ⁿ selected from the group consisting of an alkali metal, an alkaline earth metal, a

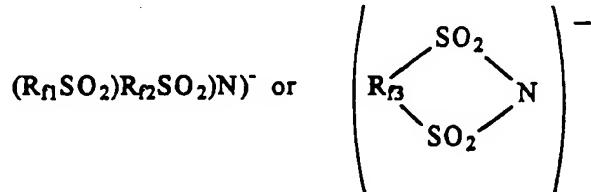
transition metal, a rare earth metal, a group IIB metal, a Group IIIB metal, and tetraalkylammonium.

7. The composition of claim 6, wherein the cation is selected from the group consisting of Li^+ , Na^+ , Ca^{+2} , Ba^{+2} , Al^{+3} , Eu^{+3} , Sm^{+3} , $(\text{C}_2\text{H}_5)_4\text{N}^+$ and $(\text{CH}_3)_4\text{N}^+$.

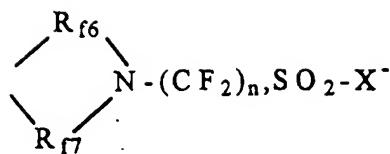
8. The composition of claim 1, wherein the surfactant salt is selected from the group consisting of $(\text{C}_8\text{F}_{17}\text{SO}_2)\text{N}^+(\text{SO}_2\text{CF}_3)\text{Li}^+$, $(\text{C}_4\text{F}_9\text{SO}_2)_2\text{N}^+\text{Li}^+$,
10 $(\text{C}_8\text{F}_{17}\text{SO}_2)_2\text{NLi}^+$, $(\text{C}_8\text{F}_{17}\text{SO}_2)\text{N}^+(\text{SO}_2\text{C}_4\text{F}_9)\text{Li}^+$, and $(\text{C}_4\text{F}_9\text{SO}_2)\text{N}^+(\text{SO}_2\text{CF}_3)\text{Li}^+$.

9. The composition of claim 1, wherein the molar ratio of conductive salt to surfactant salt is between about 99:1 and about 90:10.

15 10. The composition of claim 1, wherein the conductive salt has:
a cation selected from the group consisting of an alkali metal, alkaline earth metal, a Group IIB metal, a Group IIIB metal, a transition metal, a rare earth metal, tetraalkylammonium and trialkylammonium; and has
an anion selected from the group consisting of NO_3^- , Br^- , Γ , BF_4^- , PF_6^- ,
20 AsF_6^- , ClO_4^- , SbF_6^- and $\text{R}_f^0\text{SO}_3^-$, in which R_f^0 is a perfluoroalkyl group having between 1 and 12 carbon atoms;
an anion of the formula



25 in which R_{f1} and R_{f2} are each independently a straight or branched perfluoroalkyl group of 1 to 12 carbon atoms, and R_{f3} is a perfluoroalkylene moiety of 2 to 4 carbon atoms optionally substituted by a straight or branched perfluoroalkyl group of 1 to 2 carbon atoms, with R_{f3} having a total of up to 4 carbon atoms;
an anion having a formula $\text{R}_{f4}\text{R}_{f5}\text{N}-(\text{CH}_2)_n\text{SO}_2-\text{X}$;



in which X' is $-\text{O}^-$, $-\text{NSO}_2\text{R}_{f4}'$ or

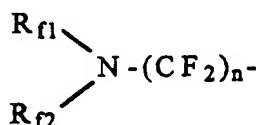


Z is $-\text{CF}_2^-$, $-\text{O}^-$,



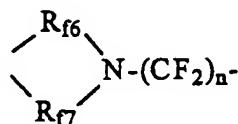
10

or $-\text{SF}_4^-$; R_{f4} and R_{f5} independently, are $-\text{C}_m\text{F}_{2m+1}'$ or $-(\text{CF}_2)_q-\text{SO}_2-\text{X}'$; R_{f16} and R_{f17}' independently, are $-\text{C}_m\text{F}_{2m+1}'$ $-(\text{CF}_2)_4-\text{SO}_2-\text{X}'$,



or

15



R_{f8} is $-\text{C}_m\text{F}_{2m+1}'$ or $-(\text{CF}_2)_q-\text{SO}_2-\text{X}'$; R_{f5} and R_{f7}' independently, are perfluoroalkylene moieties having the formula $-\text{CF}_{2r}$; n' is 1-4; r is 1-4; m is 1-12; and q is 1-4; a bisfluoroacylsulfonyl methide anion $\text{R}_f^{\text{II}}-\text{SO}_2-\text{C}^-(\text{R})-\text{SO}_2-\text{R}_f^{\text{III}}$ in

20 which R_f^{II} and R_f^{III} independently, are perfluoroalkyl groups having between 1 and 12 carbon atoms, and X is H, Br, Cl. I, an alkyl group having between 1 and 20 carbon atoms, aryl, or alkaryl; and a tris-(perfluoroalkylsulfonyl)methide anion of the formula $-\text{C}(\text{SO}_2\text{R}_f^{\text{II}})(\text{SO}_2\text{R}_f^{\text{III}})(\text{SO}_2\text{R}_f^{\text{IV}})$ in which R^{III} , R_f^{III} , and R_f^{IV} , independently, are perfluoroalkyl groups having between 1 and 12 carbon atoms.

wherein M^{+n} is a cation with a valence equal to n;

n is from 1 to 4;

R_f is a straight or branched perfluoroalkyl group of 1 to 12 carbon atoms, a perfluorocycloalkyl group or a perfluorocycloalkyl perfluoroalkyl group of 4-7

5 ring carbon atoms and 1-4 carbon atoms in the alkyl chain, which perfluoroalkyl or perfluorocycloalkyl chain may optionally contain catenary heteroatoms; and

R_f' is a straight or branched perfluoroalkyl group of 1 to 8 carbon atoms, a perfluorocycloalkyl group or a perfluorocycloalkyl perfluoroalkyl group of 4-7

ring, carbon atoms and 1-4 carbon atoms in the alkyl chain, which perfluoroalkyl

10 or perfluorocycloalkyl chain may optionally contain catenary heteroatoms, wherein R_f and R_f' have a total of at least 5 carbon atoms; and

wherein the molar ratio of conductive salt to surfactant salt is between about 99.9:0.1 to about 75:25.

15 15. The system of claim 14, wherein the conductive salt is different from the surfactant salt.

16. The system of claim 14, wherein the surfactant salt, R_f and R_f' have a total of at least 8 carbon atoms.

20 17. The system of claim 14, wherein the molar ratio of conductive salt to surfactant salt is between about 99:1 and about 90:10.

18. The system of claim 14, wherein the surfactant salt has a cation M^{+n} selected from the group consisting of an alkali metal, an alkaline earth metal, a transition metal, a rare earth metal, a group IIB metal, a Group IIIB metal, tetraalkviammonium, trialkviammonium and a proton.

19. The system of claim 18, wherein the cation is selected from the group consisting of Li^+ , Na^+ , Ca^{+2} , Ba^{+2} , Al^{+3} , Eu^{+3} , $(C_2H_5)_4N^+$ and $(CH_3)_4N^+$.

wherein M^{+n} is a cation with a valence equal to n;

n is from 1 to 4;

R_f is a straight or branched perfluoroalkyl group of 1 to 12 carbon atoms, a perfluorocycloalkyl group or a perfluorocycloalkyl perfluoroalkyl group of 4-7 ring carbon atoms and 1-4 carbon atoms in the alkyl chain, which perfluoroalkyl or perfluorocycloalkyl chain may optionally contain catenary heteroatoms; and

10 R_{f'} is a straight or branched perfluoroalkyl group of 1 to 8 carbon atoms, a perfluorocycloalkyl group or a perfluorocycloalkyl perfluoroalkyl group of 4-7 ring, carbon atoms and 1-4 carbon atoms in the alkyl chain, which perfluoroalkyl or perfluorocycloalkyl chain may optionally contain catenary heteroatoms, wherein R_f and R_{f'} have a total of at least 5 carbon atoms; and

wherein the molar ratio of conductive salt to surfactant salt is between about 99.9:0.1 to about 75:25.

15 15. The system of claim 14, wherein the conductive salt is different from the surfactant salt.

16. The system of claim 14, wherein the surfactant salt, R_f and R_{f'} have a total of at least 8 carbon atoms.

20 17. The system of claim 14, wherein the molar ratio of conductive salt to surfactant salt is between about 99:1 and about 90:10.

18. The system of claim 14, wherein the surfactant salt has a cation M⁺ⁿ selected from the group consisting of an alkali metal, an alkaline earth metal, a transition metal, a rare earth metal, a group IIB metal, a Group IIIB metal, tetraalkviammonium, trialkviammonium and a proton.

30 19. The system of claim 18, wherein the cation is selected from the group consisting of Li⁺, Na⁺, Ca⁺², Ba⁺², Al⁺³, Eu⁺³, (C₂H₅)₄N⁺ and (CH₃)₄N⁺.

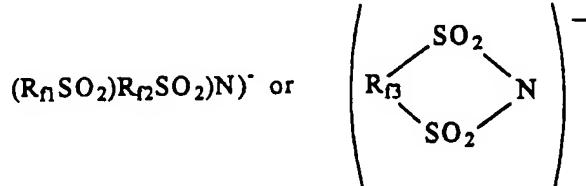
20. The system of claim 14, wherein the surfactant salt is a member selected from the group consisting of $(C_8F_{17}SO_2)N^-(SO_2CF_3) Li^+$, $(C_4F_9SO_2)_2N^- Li^+$, $(C_8F_{17}SO_2)N^-(SO_2C_4F_9) Li^+$, $(C_8F_{17}SO_2)_2N^- Li^+$, and $(C_4F_9SO_2)N^-(SO_2CF_3) Li^+$.

5 21. The system of claim 14, wherein the electrolyte composition comprises:

- (a) a conductive salt at a concentration from about 0.5 to 1.5 mole per liter; and
- (b) 10 a surfactant salt at a concentration from about 10 to 100 millimole per liter.

22. The system of claim 14, wherein the conductive salt has:
 a cation selected from the group consisting of an alkali metal, alkaline earth metal, a Group IIB metal, a Group IIIB metal, a transition metal, a rare earth metal,
 15 tetraalkylammonium; and
 an anion selected from the group consisting of NO_3^- , Br^- , I^- , BF_4^- , PF_6^- ,
 AsF_6^- , CIO_4^- , SbF_6^- and $R_f^0SO_3^-$, in which R_f^0 is a perfluoroalkyl group having between 1 and 12 carbon atoms;

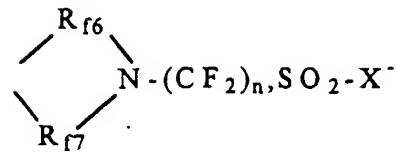
an anion of the formula



20 in which R_{f1} , and R_{f2} are each independently a straight or branched perfluoroalkyl group of 1 to 12 carbon atoms;

and R_{f3} , is a perfluoroalkylene moiety of 2 to 4 carbon atoms optionally substituted by a straight or branched perfluoroalkyl group of 1 to 2 carbon atoms,
 25 with R_{f3} having a total of up to 4 carbon atoms;

an anion having a formula $R_{f4}R_{f5}N-(CH_2)_nSO_2-X$;



in which X' is $-\text{O}^-$, $-\text{NSO}_2\text{R}_{f4}'$ or

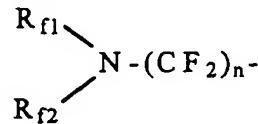


Z is $-\text{CF}_2^-$, $-\text{O}^-$,



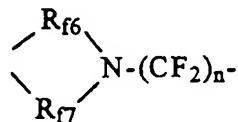
10

of $-\text{SF}_4^-$; R_{f4} and R_{f5} , independently, are $-\text{C}_m\text{F}_{2m+1}$, or $-(\text{CF}_2)_q-\text{SO}_2-\text{X}$; R_{f6} and R_{f7} , independently, are $-\text{C}_m\text{F}_{2m+1}$, $-(\text{CF}_2)_q-\text{SO}_2-\text{X}'$,



15

or



R_{f8} is $-\text{C}_m\text{F}_{2m+1}$, or $-(\text{CF}_2)_q-\text{SO}_2-\text{X}'$; R_{f6} and R_{f7} , independently, are perfluoroalkylene moieties having the formula $-\text{C}_r\text{F}_{2r}$; n' is 1-4; r is 1-4; m is 1-12; and q is 1-4; a bisfluoroalkylsulfonyl methide anion $\text{R}_f^{\text{II}}-\text{SO}_2-\text{C}^-(\text{R})-\text{SO}_2-\text{R}_f^{\text{III}}$ in
20 which R_f^{II} , and R_f^{III} , independently, are perfluoroalkyl groups having between 1 and 12 carbon atoms, and X is H, Br, Cl, I, an alkyl group having between 1 and 20 carbon atoms, aryl, or alkaryl; and a tris-(perfluoroalkylsulfonyl)methide anion of

the formula $-C(SO_2R_f^{II})(SO_2R_f^{III})(SO_2R_f^{IV})$ in which R_f^{II} , R_f^{III} , and R_f^{IV} , independently, are perfluoroalkyl groups having between 1 and 12 carbon atoms.

23. The system of claim 22, wherein the conductive salt is lithium
5 hexafluorophosphate, lithium bis(trifluoromethanesulfonyl)imide or a mixture thereof.

24. The system of claim 14, being a battery or rechargeable battery.
10 25. The battery or rechargeable battery of claim 24, comprising a lithium intercalated carbon anode and a metal oxide cathode.

1/3

FIG. 1

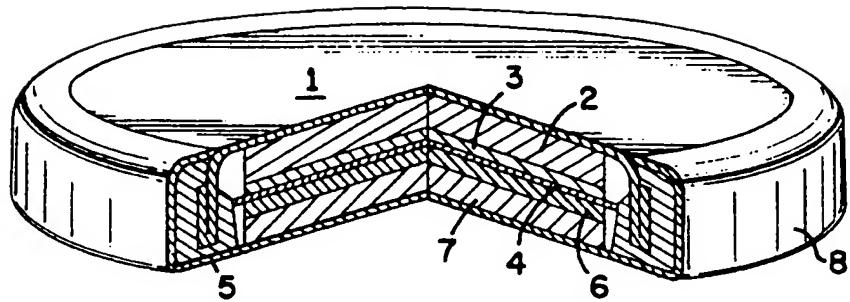


FIG.2

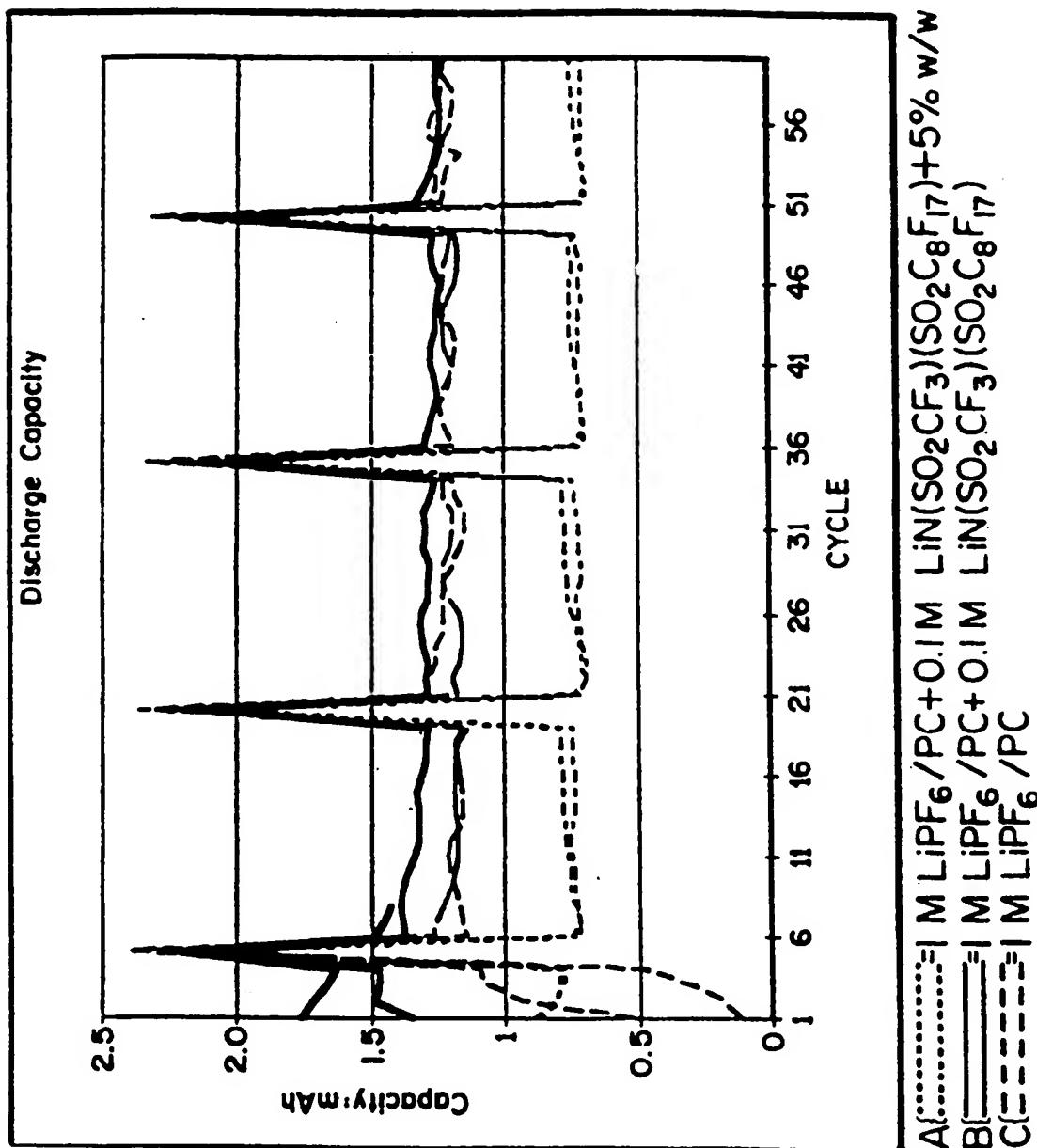
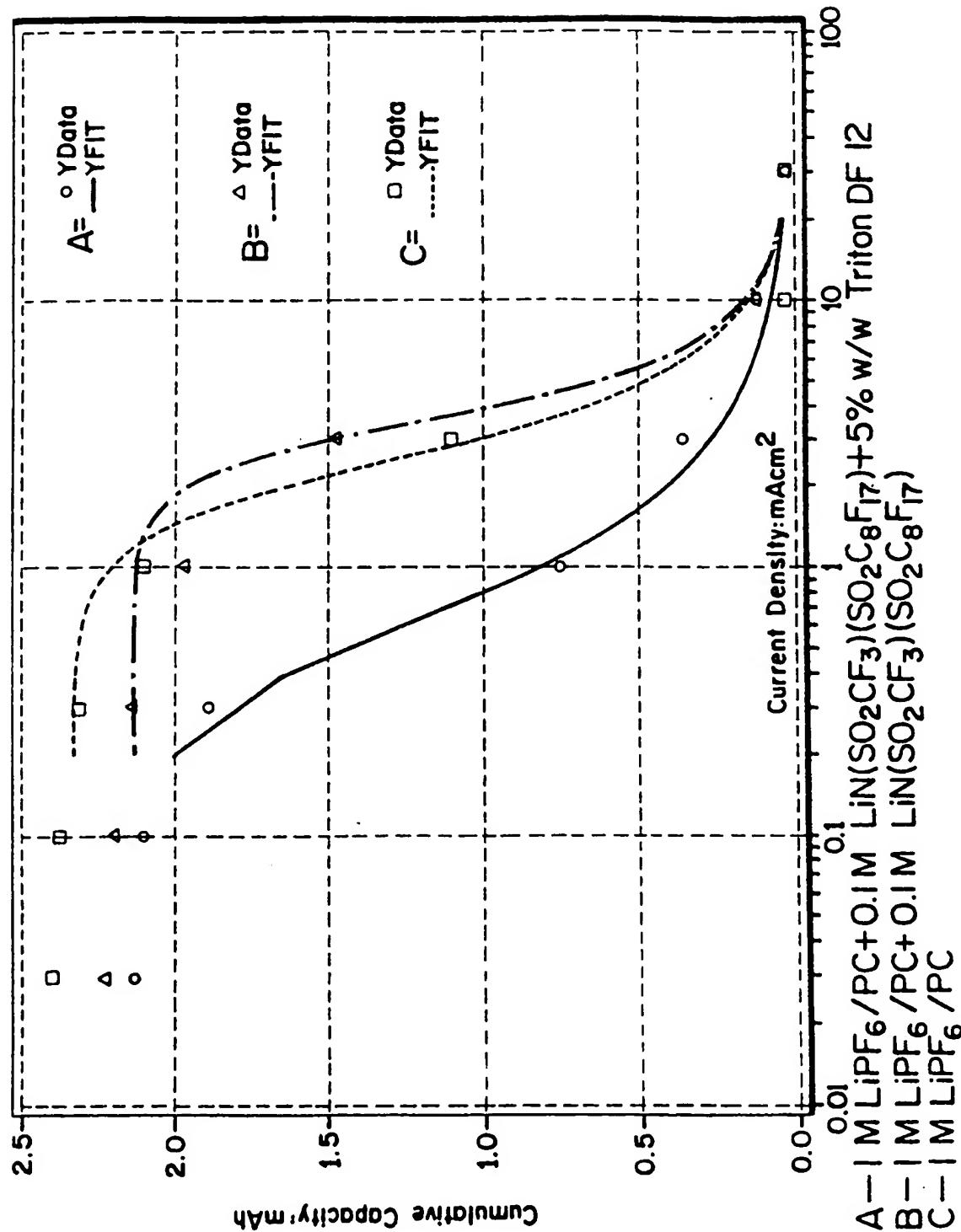


FIG. 3



INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/US 98/11708

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01M10/40 C07C311/48

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	<p>WO 97 11504 A (MINNESOTA MINING & MFG) 27 March 1997 cited in the application</p> <p>see page 5, line 3-25; claims 1,2,4-7 see page 11, line 27 - page 12, line 25 see page 15, line 5-18 see page 6, line 28 - page 10, line 15 see claims 1,2,4-7</p> <p>---</p> <p>DE 22 39 817 A (BAYER AG) 21 February 1974 see page 4, paragraph 4; claims 1-5</p> <p>---</p> <p>-/-</p>	1,3-8, 10-14, 16, 18-20, 22-25
Y		1-25

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

5 October 1998

12/10/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

De Vos, L

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/11708

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	FR 2 704 099 A (CENTRE NAT ETD SPATIALES) 21 October 1994 see page 3, line 22 - page 4, line 4 see page 6, line 10 - page 9, line 6; claims 1-19 ----	2,9,15, 17,21
A	EP 0 571 832 A (BAYER AG) 1 December 1993 see page 2, line 16 - page 3, line 49; claims 1-8 see page 7; line 3 - page 8, line 2; claims 1-8 ----	1-9
A	PATENT ABSTRACTS OF JAPAN vol. 097, no. 008, 29 August 1997 & JP 09 092280 A (HITACHI LTD), 4 April 1997 see abstract ----	1,2,14, 15
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 375 (E-1397), 14 July 1993 & JP 05 062690 A (YUASA CORP), 12 March 1993 see abstract ----	1-3,6-8, 10,11, 13-16
A	PATENT ABSTRACTS OF JAPAN vol. 096, no. 002, 29 February 1996 & JP 07 282851 A (SONY CORP), 27 October 1995 see abstract ----	1,2,9, 14,15
A	EP 0 466 483 A (AUSIMONT SPA) 15 January 1992 see claims 9-27 -----	1,14

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern.	Application No
PCT/US 98/11708	

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9711504	A	27-03-1997	US	5652072 A	29-07-1997
			US	5691081 A	25-11-1997
			EP	0852072 A	08-07-1998
DE 2239817	A	21-02-1974	NONE		
FR 2704099	A	21-10-1994	NONE		
EP 0571832	A	01-12-1993	DE	4217366 A	02-12-1993
			CA	2096816 A	27-11-1993
			DE	59301437 D	29-02-1996
			DK	571832 T	13-05-1996
			ES	2085075 T	16-05-1996
			JP	6116229 A	26-04-1994
			US	5502251 A	26-03-1996
EP 0466483	A	15-01-1992	IT	1246357 B	17-11-1994
			CA	2046949 A	13-01-1992
			DE	69113695 D	16-11-1995
			DE	69113695 T	15-05-1996
			JP	6128216 A	10-05-1994
			US	5374770 A	20-12-1994
			US	5241110 A	31-08-1993